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Short communication

SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE CARBONATES OBTAINED DURING THE REACTION OF UREA WITH LANTHANIDE(III) SALTS AT HIGH TEMPERATURE

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Lanthanide(III) carbonates, $Ln_2(CO_3)_3 \cdot nH_2O$ (Ln = Y, La, Ce or Sm; n = 4–6) were obtained during the reaction of aqueous solutions of LnX_3 ($X^- = Cl^-$ or NO_3^-) with urea at ~ 80°C for several hours. The reaction products were characterized via elemental analysis and infrared spectroscopy. The infrared spectra clearly show the characteristic bands due to carbonate ions. General reaction equations describing the formation of lanthanide carbonates were proposed.

Key words: lanthanide(III) ions; urea; infrared spectra

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НА КАРБОНАТИ НА ЛАНТАНИДИ ДОБИЕНИ ВО РЕАКЦИЈА НА УРЕА СО СОЛИ НА ЛАНТАНИДИ(III) НА ВИСОКА ТЕМПЕРАТУРА

Карбонатите на лантаниди(III), $Ln_2(CO_3)_3 \cdot nH_2O$ (Ln = Y, La, Ce или Sm; n = 4-6) беа добиени при реакција на водни раствори на LnX_3 ($X^- = Cl^-$ или NO_3^-) со уреа на 80 °C за време од неколку часови. Карактеризација на продуктите на реакцијата беше направена со елементарна анализа и инфрацрвена спектроскопија. На инфрацрвените спектри беа јасно видливи карактеристичните ленти за карбонатните јони. Предложени се општи равенки кои го опишуваат формирањето на карбонатите на лантаниди.

Клучни зборови: карбонати на лантаниди(III); инфрацрвена спектроскопија; елементарна анализа

INTRODUCTION

Stable compounds have been isolated during the reaction of urea, as a neutral oxygen-containing molecule, with uranyl ions, and these compounds were well characterized [1–3]. The reactions of rare earth metal ions with urea and some of its related complexes have been carried out [4–9], and solid metal-urea complexes have been isolated and characterized using elemental analysis, electronic and IR spectra, as well as thermal analysis. Lanthanide (Y, La, Ce, Pr, Nd, Sm, Gd and Dy) complexes using substituted ureas and thioureas as ligands, and lanthanide mixed complexes using urea and phenylthioureas, have been prepared and characterized [10]. The infrared spectra of all of these complexes showed that urea molecule behaves as a monodentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom. The common features of all these investigations are the synthesis and the study of the properties of the isolated metal-urea complexes obtained during the reaction of urea with these metal ions at room (or lower) temperature. But none of them were designed to investigate the nature of the reaction of urea with these metal ions at high temperatures.

Studies on the nature of the reaction of urea with metal ions at high temperature are very rare in the literature, and the available publications describe an interesting feature: the reaction products depend not only on the type of metal ions but also on the metal salt used in these reaction [11–16].

The present study was undertaken to investigate the nature of the reaction products obtained during the reaction of urea with lanthanide(III) ions, LnX_3 (Ln = Y, La, Ce and Sm; X^- = Cl^- or NO_3^-) in aqueous solution at ~ 80°C. The reaction products were isolated as solids, and characterized by elemental analysis, infrared spectra, and gravimetric analysis to determine the water content.

EXPERIMENTAL

Reagent grade chemicals were used throughout. $Ln_2(CO_3)_3{\cdot}nH_2O$ (Ln = Y, La, Ce and Sm; n = 4 – 6) were prepared by mixing aqueous solutions (100 ml) of 0.01 M of the respective lanthanide metal salts, $LnX_3{\cdot}nH_2O$ (X^- = Cl^- or NO_3^-; n = 6 or 7) with a volume of 100 ml of 0.1 M of urea. The mixtures were heated to ~ 80 °C for 2–4 h in a water bath. The precipitated white compounds were filtered out, washed several times with hot water, dried at 80°C in an oven for 2 h and then in *vacuo* over silica gel. The yields of the obtained lanthanide carbonates varied in the range 93 to 82%, depending upon the type of metal and the counter ions associated with the metal ion. The carbonate content in $Ln_2(CO_3)_3{\cdot}nH_2O$ was determined by dissolving a weighted sample of the products in excess standard HCl; the excess of HCl was determined by titration with standard sodium carbonate. Lanthanide metals Y, La and Sm were determined gravimetrically as sesquioxides, Ln_2O_3, while cerium was determined as CeO_2. The infrared spectra of urea and lanthanide carbonates were recorded in KBr discs using a Perkin-Elmer 1430 Ratio-Recording Infrared Spectrophotometer and Genesis II FT-IR.

RESULTS AND DISCUSSION

The elemental analysis for $Ln_2(CO_3)_3{\cdot}nH_2O$ obtained during the reaction of urea with the respective metal chloride or nitrate were almost identical, and indicated the absence of nitrogen. Analysis of the products obtained using metal nitrates is as follows (Table 1).

The reactions of aqueous solutions of urea and lanthanide(III) salts, LnX_3 (Ln = Y, La, Ce and Sm; X^- = Cl^- or NO_3^-) produce white solid products of lanthanide(III) carbonates. The infrared spectra of urea and the carbonates of Y(III) and Ce(III) are shown in Fig. 1, while those of La(III) and Sm(III) carbonates are given in Fig. 2. Band assignments of all of infrared bands observed in the spectra of carbonates are given in Table 2.

The infrared spectra of all obtained products show no bands due to coordinated urea, and a group of bands characteristic for ionic carbonate [17]. These bands are observed above 1400 cm^{-1} and around 1075 cm^{-1} due to the stretching vibrations, ν(C–O), and around 850 and 730 cm^{-1} due to the bending motions, δ(OCO), associated with carbonate ions. The assignment of the bands to these frequencies agrees quite well with those generally known for the ionic carbonate. The infrared spectrum obtained for the ionic carbonate (CO_3^{2-}) is almost the same as those of the reaction products. Based on these facts, and along with the data obtained from elemental analysis and the determination of CO_3^{2-} with HCl, the reaction products obtained were identified as $Ln_2(CO_3)_3{\cdot}nH_2O$, (Ln = Y, La, Ce or Sm and n = 4–6).

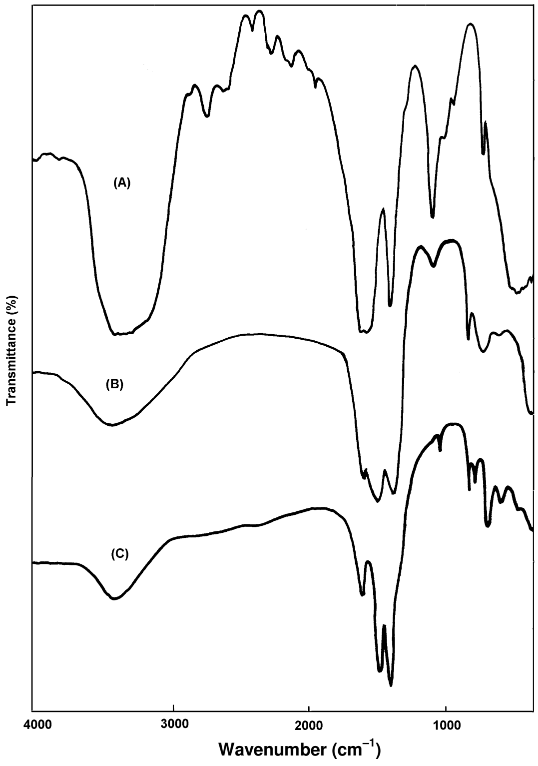

Fig. 1. Infrared spectra of (A) Urea, (B) $Y_2(CO_3)_3{\cdot}6H_2O$ and $Ce_2(CO_3)_3{\cdot}6H_2O$

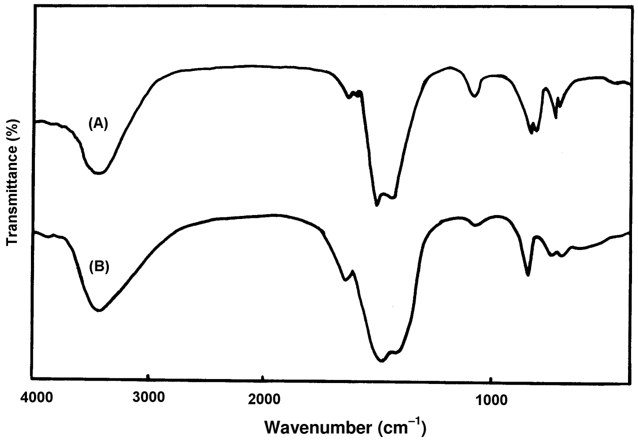

Fig. 2. Infrared spectra of (A) $Sm_2(CO_3)_3 \cdot 4H_2O$ and (B) $La_2(CO_3)_3 \cdot 5H_2O$

Table 1

Elemental analysis data of $Ln_2(CO_3)_3 \cdot nH_2O$

Compunds (Mr)	% C		% H		% M		% CO_3	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Y_2(CO_3)_3 \cdot 6H_2O$ (466)	7.72	7.63	2.57	2.64	38.15	37.84	38.62	38.04
$La_2(CO_3)_3 \cdot 5H_2O$ (548)	6.56	6.37	1.82	2.03	50.69	50.72	32.84	32.62
$Ce_2(CO_3)_3 \cdot 6H_2O$ (568)	6.33	6.24	2.11	2.31	49.33	50.01	31.69	31.35
$Sm_2(CO_3)_3 \cdot 4H_2O$ (553)	6.52	6.47	1.45	1.61	54.38	54.19	32.55	32.60

Table 2

Infrared frequencies (cm^{-1}) and assignments of $Ln_2(CO_3)_3.nH_2O$ *obtained from the reaction of different* LnX_3 *salts (Ln = Y, La, Ce and Sm;* $X^- = Cl^-$ *or* NO_3^-*) with urea at high temperature*

Assignments	Frequency, cm^{-1}				
	$Y_2(CO_3)_3 \cdot 6H_2O$	$La_2(CO_3)_3 \cdot 5H_2O$	$Ce_2(CO_3)_3 \cdot 6H_2O$	$Sm_2(CO_3)_3 \cdot 4H_2O$	$CaCO_3$
ν(O–H); H_2O	3442	3437	3450	3446	–
δ(H2O); H_2O	1628, 1615	1634, 1623	1642, 1615	1640, 1610	–
ν(C–O); CO_3^{2-}	1507, 1420 1065	1470, 1412 1066	1485, 1420 1071	1497, 1452 1087	1492, 1429 1080
δ(OCO); CO_3^{2-}	872 728	857 746, 705	857, 829 742, 708	859, 842 732, 720	879 706

Previous studies [11–16] indicated that the nature of the reaction products obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ions and the metal salt used. However, in some cases [16] we have obtained the same product, $MnCO_3 \cdot H_2O$, regardless of the counter ions associated with the manganese(II) ions. In this investigation we have obtained the same reaction products, $La_2(CO_3)_3 \cdot nH_2O$ by using lanthanide(III) metal (Y, La, Ce and Sm) ions associated with different counter ions, Cl^- or NO_3^-. The role of Ln(III) ions in decomposing the coordinated urea at high temperature may be understood in the following manner:

At room temperature, Y(III) and lanthanide (La, Ce and Sm(III)) ions react with urea to form the complex, $Ln(urea)_3X_3$ [4–7]. At high temperature, the following reactions may take place:

$$2[La(U)_3X_3] + 14H_2O \xrightarrow{\text{ca.}80\ ^{o}C} La_2(CO_3)_3{\cdot}5H_2O + 3CO_2 + 6NH_4X + 6NH_3$$

$$2[Sm(U)_3X_3] + 13H_2O \xrightarrow{\text{ca.}80\ ^{o}C} Sm_2(CO_3)_3{\cdot}4H_2O + 3CO_2 + 6NH_4X + 6NH_3$$

$$2[Ln(U)_3X_3] + 15H_2O \xrightarrow{\text{ca.}80\ ^{o}C} Ln_2(CO_3)_3{\cdot}6H_2O + 3CO_2 + 6NH_4X + 6NH_3$$

(Ln = Y and Ce; X = Cl^- or NO_3^-)

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